Renewable biofuel additives from the ozonolysis of lignin

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Abstract

In this investigation ozonolysis in the presence of ethanol was used to depolymerise lignin, resulting in a low conversion of oxygenated aromatics over short reaction times, or a range of saturated esters over 24 hours. Short chain oxygenates can be used as fuel additives, displacing a percentage of a hydrocarbon fuel while leading to improvement in some of the fuel properties. The utility of the resulting bio-oils was therefore assessed by blending with a range of fuels. Guaiacol, a potential antioxidant, was formed over short reaction times and was found to be completely miscible with low-sulphur petrol (ULSP), diesel, aviation kerosene and rapeseed methyl ester. The mainly aliphatic proportion of the bio-oil produced over 24 hours could be blended with the fuels replacing a maximum of 12 – 17 wt.% of the hydrocarbon fuel.

Keywords lignin, ozone, depolymerisation, biofuel, aviation

1 Introduction

An increasing awareness of the negative environmental cost associated with the combustion of fossil fuels and concerns over the geopolitical instability of the main oil producing regions is driving the development of renewable biofuels. Biofuels produced from cellulosic resources, which can be blended without major infrastructure changes, are a key technology that will aid in reducing the use of fossil fuels. Promising sources of cellulosic material are waste food, agricultural residues and non-food crops that can be grown on marginal land. Plants such as switchgrass, for example, can be cultivated on land that is not fit for edible crop production, thus removing any competition with food (Schaidle et al., 2011). The use of lignocellulosic biomass as a feedstock for renewable fuels and additives has enormous potential due to its abundance and chemical flexibility; it has also been reported that cultivation is less labour and water intensive than for other forms of biomass (Berndes et al., 2001; Patwardhan et al., 2011). Lignocellulose is composed of cellulose, hemicellulose and lignin; the relative proportions of which vary according to the type of plant. Grasses contain relatively large proportions of celluloses whilst hard and softwoods contain more lignin.

A huge research and development effort is underway to develop sustainable transport fuels from cellulose and currently there are a number of pilot scale lignocellulose-to-ethanol plants around the world (Kamm et al., 2010; Weber et al., 2010). While cellulose has been heavily exploited in the production of fuels, the lignin produced as part of the process has not been so well developed. Lignin is a robust biopolymer, accounting for between 10-25% by weight and up to 40% of the energy content of lignocellulosic biomass and is relatively underused considering the abundance of this natural product (Berndes et al., 2001; Kutscha & Gray, 1970).

Lignin is comprised of interlinked *p*-hydroxyphenylpropane monomeric units, or monolignols. The three main monolignols are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Davin & Lewis, 2005; Kleinert & Barth, 2008a). Along with the amount of lignin in wood, the proportions of monolignols vary between sources; softwoods are known to contain a higher percentage of lignin than hardwoods, however softwood lignin is dominated by guaiacyl units whereas hardwoods have approximately equal amounts of guaiacyl and syringyl units (Pandey & Kim, 2011). Linkages between monolignols are varied and include C-C and C-O bonds, however the dominant linkages are *β*-O-4 aryl ethers (Pandey & Kim, 2011). Separation of lignin from celluloses and subsequent degradation of the lignin polymer into potentially useful products is challenging and can be energy intensive (Kutscha & Gray, 1970). Thus, whilst celluloses are widely viewed as valuable renewable feedstocks for fuel production, lignin tends to be seen as a contaminant and its removal represents a high proportion of energy usage in cellulosic processing (Alonso et al., 2010).

To unlock the chemical potential lignin must be depolymerised. Several methods have been presented in the literature for the depolymerisation of lignin; these include enzymatic (ten Have & Teunissen, 2001) thermal or catalytic degradation (Kleinert & Barth, 2008b; Korpi et al., 2006; Kuznetsov et al., 2008; Pandey & Kim, 2011; Yan et al., 2008; Yuan et al., 2010), microwave irradiation (Kappe, 2004; Ouyang et al., 2010) and ozonolysis.

Ozonolysis has been used as a technique for the delignification of wood and has been reported to oxidatively degrade the lignin polymer structure through this process (Mamleeva et al., 2009; Miura et al., 2012; Travaini et al., 2013). Ozonolysis is an attractive oxidation technique due to the mild reaction conditions needed. There are no toxic residues left behind as any residual ozone in the system will quickly decompose back to O_2 due to its

short half-life. Ozone can also be easily generated on site where and when it is required, reducing transport costs. Several groups have conducted kinetic studies into the reaction of lignin with ozone, mostly using water-soluble lignosulfonates; most data reported are kinetic in nature, including reaction rates, ozone consumption and ozone demand (Mamleeva et al., 2009; Ramos et al., 2009). Few papers describe in any detail the products formed, however, many report the eventual destruction of aromatic rings and when the ozonation is carried out in the presence of water the formation of some organic acids such as oxalic, glycolic and malonic are observed (Quesada et al., 1997).

The further development and production of cellulosic biofuels will increase the amount of lignin available for chemical processing dramatically. As such any eventual use for depolymerised lignin must be of a sufficient size to match production. One such use is as a blending agent or additive in transport fuels. In this investigation the ozonolysis of lignin, using an alcohol co-solvent, was examined as a method of producing oxygenated components that could be blended with transport fuels further displacing a certain amount of the fossil fuel. It has been established that the addition of oxygenated species as fuel additives can be beneficial in terms of emissions or fuel performance in road transport fuels and it was hoped that the addition of these lignin derived components would not significantly alter other key physical properties of the fuels.

2 Material and Methods

2.1 Materials

Lignin in these experiments refers to alkali lignin (low sulfonate content) purchased from Sigma Aldrich which was used without any additional purification. The M_w average was

approximately 10,000 g mol^{-1} and the lignin had a sulphur content of 4%. All other chemicals were purchased from Sigma Aldrich and used without any additional purification.

2.2 Analytical techniques

Elemental compositions were obtained using an Exeter Analytical Inc. CE-440 Elemental Analyser in CHN mode. GC-MS analysis was carried out using an Agilent 7890A Gas Chromatograph equipped with a capillary column (30 m × 0.250 mm internal diameter) coated with HP-5 ([5% Phenyl]-methylpolysiloxane) stationary phase (0.25 µm film thickness) and a He mobile phase (flow rate: 1.2 ml/min) coupled with an Agilent 5975C inert MSD with Triple Axis Detector.

NMR analysis was carried out using a Brüker Advance (300.22 MHz) spectrometer at 303 K in CD_3OD as solvent. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak and coupling constants are reported in Hertz. ESI-MS analysis was recorded on a Bruker Daltonic microTOF electrospray time-of-flight (ESI-TOF) mass spectrometer coupled to an Agilent 1200 LC system as an autosampler. 10 µL of sample was injected into a 30:70 flow of water:acetonitrile at 0.3 mL/min into the mass spectrometer.

The energy content was measured using a Parr 1341 Plain Oxygen Bomb Calorimeter, in accordance with ASTM D240. Flash point analysis was carried out using a Stanhope Seta TAG closed cup flash point tester, in accordance with ASTM D3934. Cloud points were measured by cooling the samples by 1 °C min^{-1} and holding at each temperature for 10 minutes, observing any solid formation by eye. The kinematic viscosities were measured with calibrated Canon-Fenske Routine Viscometers No. 75 and 150, in accordance with standard test methods set out in ASTM D445 and ISO 3104 at 40 °C or -20 °C where appropriate.

2.3 Ozonolysis of lignin

Ozone was generated using a Hydroponics Mini Ozone Generator providing an ozone flow rate of 300 mg h^{-1}. A large round-bottomed flask was charged with 1 g of lignin and 100 mL solvent. The reaction was stirred and ozone was passed through in a flow of air for the desired time at atmospheric pressure and temperature. The outflow gases were passed through a reservoir of aqueous potassium iodide to react any remaining ozone. At the end of the reaction, residual solids were filtered off and the solvent was removed under reduced pressure to yield the bio-oil which was analysed by the various analytical techniques.

2.4 Miscibility studies

Depolymerised lignin (2.5 wt. %) was added to a sample vial and weighed to four decimal places. The fuel (roughly 2 ml depending on the amount of DPL used) was added to the vial with a stir bar and the vial sealed. The vial was then held at 65 °C for 1 hour with stirring, after which the vial was allowed to cool, the resulting fuel was collected and the remaining solid washed with diethyl ether. The vials were then dried in an oven held at 50 °C for 2 hours prior to weighing. All fuels were examined at least three times and the standard deviation was found to be no higher than 4% for any sample.

To determine the maximum blend level the DPL (1:1 weight ratio) was added to the parent fuel and the resulting mixture stirred over 24 hours at room temperature in a sealed vessel. The fuel was removed leaving behind a thick tar in all cases. The tar was washed with diethyl ether, dried under a flow of argon for 10 minutes and remaining tar was weighed to calculate the amount of DPL solubilised into the fuel.

3 Results and Discussion

3.1 Characterization of the depolymerised lignin

It has been established that the use of ozone for the delignification of lignocellulosic biomass leads to some degradation of the lignin biopolymer (Mamleeva et al., 2009). By harnessing this ability, it was hoped that ozone could be used to depolymerise lignin to produce compounds suitable for blending with petrochemical fuels. Ozonolysis experiments were conducted at atmospheric temperatures and pressures in standard laboratory glassware. Originally three solvents were examined, ethanol, *n*-butanol and hexane. After a 24 hour reaction time, the ozonolysis reactions produced pale yellow bio-oils and gave off the distinctive fragrance associated with esters. Only 38% of the solid lignin had reacted when ozonised in *n*-butanol, while 86% had in ethanol. No reaction was observed in hexane except that of the solvent being oxidised. It is probable that protic solvents aid ozonolysis due to their ability to interact with intermediate depolymerisation species. It is also possible that the lack of reaction in hexane results from lack of solubility of lignin in the solvent.

A greater degree of depolymerisation was observed by ESI-MS for the depolymerisation with ethanol as it was with *n*-butanol (see supporting information). While a degree of depolymerisation of the lignin was observed in the reaction performed with *n*-butanol, ozone was also oxidising the solvent. On bubbling of ozone through *n*-butanol without lignin, butyl butyrate as well as butyl ethers were observed whereas no products were recovered on the reaction between ozone and ethanol (see supporting information).

To gain a further understanding of the depolymerisation of lignin in ethanol a range of bio-oils were produced by varying the time of the ozonolysis reaction (fig. 1a).

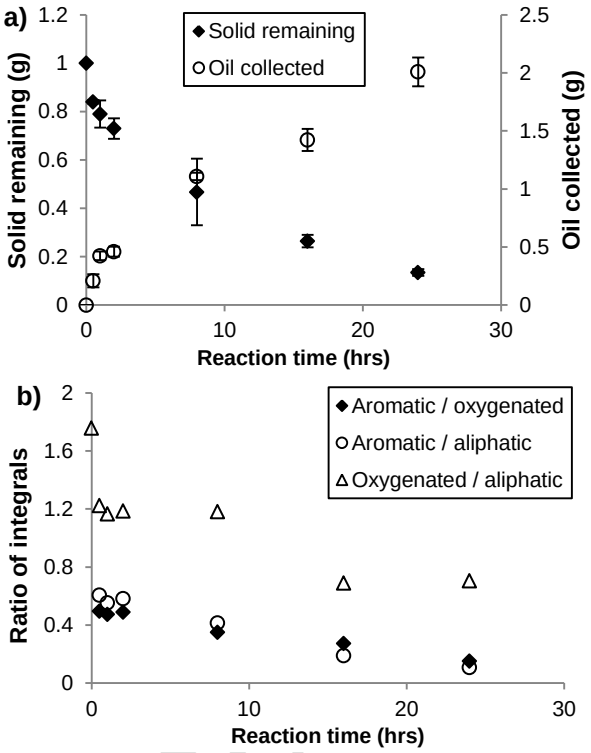

Fig. 1 a) Yields of the lignin depolymerised by ozone in the presence of ethanol, b) aromatic region (δ 6.5-7.8 ppm) compared against the α-protons adjacent to an oxygenated moiety (δ 3.4-4.8 ppm) and the aliphatic region (δ 0.5-2.1 ppm) calculated by ^{1}H NMR

On the reaction of ozone with lignin, the solid remaining slowly decreases to 14% of the original mass within 24 hours. On reaction and removal of the ethanol solvent an oxygenated product was obtained, for the lower reaction times (0.5 – 16 hours) this mixture of products was an alcohol soluble tar-like substance. A viscous bio-oil was only obtained from the reaction mixture after this point. As the lignin is being depolymerised and as both oxygen and ethanol are combined within the final products, the oil yield by weight is higher

than the original lignin, with around 2 g of oil being recovered after 24 hours from 1 g of lignin.

To further assess the products formed the oils were analysed by ^{1}H NMR (fig. 1b). While the ^{1}H NMR of lignin is vastly complex, there are three main regions which can be compared; the aliphatic (δ 0.5-2.1 ppm), the α-protons adjacent to an oxygenated moiety (δ 3.4-4.8 ppm) and the aromatic (δ 6.5-7.8 ppm). A comparison of these regions shows that the aromatics in the DPL are being destroyed as the reaction proceeds and being replaced with saturated and unsaturated oxygenates. The integral of the oxygenated region also decreases in comparison to the integral of the aliphatic region over the reaction time. This does not show that there is less oxygen in the bio-oil but rather the α-protons adjacent to the oxygen are presumably also reacting with oxygen reducing the number of these sites. To establish the identity of the more volatile components in the bio-oils the oils were analysed by GC-MS.

Analysis of the DPL formed over 24 hours showed the presence of a variety of small chain oxygenates such as short chain ethers, aldehydes and aliphatic diesters including ethyl and methyl oxalate, malonate and fumarates (A full list of the species formed is given in the supporting information). It seems likely that, along with the aromatics, oxidation of lignin by ozone forms oxalic, malonic and other diacids which are then esterified *in situ* by the ethanol. GC-MS analysis did not detect the presence of oligomers, which are evident from the ESI-MS; however it is unlikely that these larger molecules would be volatilised in the GC-MS system. Shorter reaction times yielded more substituted aromatic compounds. The major products formed under these reaction conditions are guaiacol (2-methoxyphenol), vanillin (4-Hydroxy-3-methoxybenzaldehyde), 2-methoxy-4-(1-ethenyl)phenyl acetate,

methyl methoxy(phenyl) acetate and formyl benzoate, all of which are not observed after 24 hours (see supporting information).

Fuels	**Aviation kerosene**[a]	**ULSP**[a]	**Mineral diesel**[a]	**Bioethanol**	**Biobutanol**	**Rapeseed methyl ester**[b]	**Ozonised DPL**
Density (15 °C, kg m^{-3})	0.775-0.840	0.720-0.775	0.820 – 0.845	0.794	0.814	0.883	1.232
Closed cup Flash point (°C)	38 (min)	-43 (typical)	55 (min)	14	35	182	-
Energy content (MJ/L)	34 (min)	35 (min)	37 (min)	20	29	35	18
Kinematic viscosity (mm^2 s^{-1})	8.00 max (at -20 °C)	0.37-0.44 (at 20 °C)	2.0-4.5 (at 40 °C)	1.50 (at 20 °C)	3.60 (at 20 °C)	4.89 (at 40 °C)	28 (at 40 °C)
Cloud point (°C)	-47 max	-57 (typical)	-15 - 5	-114	-90	4.5	-21

Table 1. Major fuel properties of ozonated lignin compared to a range of other fuels

[α] Value are given from the European EN 590, EN 228 and Jet A-1 standards

[b] Values dependent on the FAME profile of the biodiesel fuel, see supporting information for full fuel analysis of the RME used in this study

3.2 The application of DPL as a fuel substitute

The energy density of the pure lignin used in this study was 24.4 MJ kg^{-1}. Over the first 8 hours of ozonation this is reduced slightly as the carbon to oxygen ratio decreases. After 16

hours the energy density has reduced substantially and after 24 hours the energy density of the bio-oil is 15 MJ kg^{-1}. Due to the high oxygen content this is far lower than the common hydrocarbon fuels, though similar to bioethanol. The bio-oil formed after 24 hours has a far higher density than the comparative fuels, being more akin to glycerol, while the viscosity is a magnitude higher than most common fuels being similar to thick engine oil. Interestingly, presumably due to the abundance of short chain esters, the cloud point is well below freezing. This is lower than the biodiesel used in this study and is more akin to diesel than any of the other fuels.

While this oil has the potential to be used as a low quality heating oil, the high viscosity and low energy density would hinder the performance and there is little sense in replacing the relatively energy dense solid with this bio-oil. However, a large proportion of the DPL are esters and short chain oxygenated species. These components would be expected to have a lower viscosity and higher energy density than the total DPL oil produced in this study, as well as having a high solubility in hydrocarbon fuels. These types of oxygenates, including short chain esters, alcohols, ketones and more complex compounds have been shown to be miscible with common fuels, displacing a proportion of the original fuel, and giving enhanced fuel performance by altering the cloud point, viscosity, density, lubricity or gaseous and particulate emissions (Christensen et al., 2011a; Christensen et al., 2011b; Jenkins et al., 2013; Leedham & Caprotti, 2004; Song et al., 2003).

The extent of the DPL miscibility in a range of common hydrocarbon fuels was then examined, the compatible compounds in the DPL were analysed and the effect that these components had on the fuel properties further investigated.

3.2.1 Miscibility of the DPL additives in the hydrocarbon fuels

While the DPL produced over 24 hours of ozonolysis is a bio-oil, earlier reaction times that yield tars also produce useful products in smaller amounts. The two major products of interest are vanillin (4-Hydroxy-3-methoxybenzaldehyde) and guaiacol (2-methoxy phenol), produced between 0.5 - 5 mg g^{-1} over 0.5 - 2 hours of ozonolysis. Guaiacol is well known as a natural antioxidant (Galano et al., 2012; Sakihama et al., 2002), as is vanillin (Tai et al., 2011), with both aromatics giving a similar performance to other substituted phenolic compounds of this type. Vanillin is a crystalline solid that was not highly soluble in any of the fuels tested, however, guaiacol in its pure form is a clear liquid, which could be blended with the four fuels tested over the course of this study with no hazing, even at concentrations exceeding 10,000 ppm.

The DPL ozonated over 24 hours does not contain these aromatic components but a far greater proportion of short chain oxygenates. The DPL ozonated over 24 hours was not fully miscible with the common hydrocarbon fuels or the rapeseed methyl ester used in this study. However, the DPL is a mixture of many components so while not all the DPL is fully soluble, a proportion is. To establish what components of the DPL could be blended into the respective hydrocarbon fuels, DPL (2.5 wt%) was stirred at 65 °C for one hour in the parent fuel, the amount and type of fuel soluble components were calculated by gravimetric, ^{1}H NMR and GC-MS methods.

The solubility of the oil increases with a decrease in the aromatic portion and with an increase in the short chain oxygenated esters. For diesel and Jet A-1, whose components are reasonably similar, around 35% of the DPL formed after 16 hours is soluble, after 24 hours this increases to over 45%. This trend is also observed in the case of ultra-low suphur petrol

(ULSP), though less components of the DPL are soluble in the more volatile hydrocarbon fuel. While the DPL is predominantly aromatic the proportion of biodiesel soluble components is very low still. The solubility in the FAME increases dramatically with an increase in the oxidation and over 50% of the DPL can be solubilised in the rapeseed methyl ester after a 24 hour reaction time. All the components in the DPL are miscible with ethanol irrespective of the length of ozonolysis.

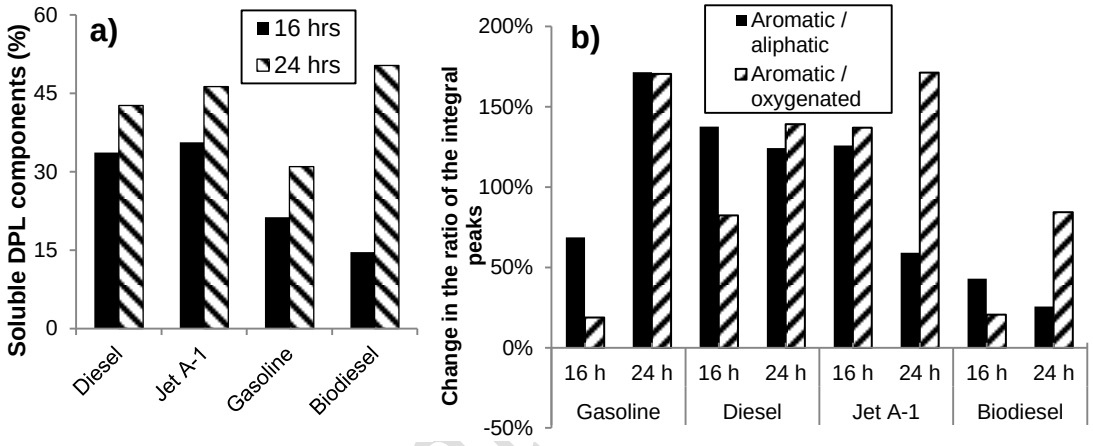

Fig. 2 a) The amount of DPL that is miscible, on mixing of 2.5 wt.% DPL in one of four major fuels, calculated by weight b) Change in the ratio of the ^{1}H NMR integrals of the aromatic region (δ 6.5-7.8) compared against the α-protons adjacent to an oxygenated moiety (δ 3.4-4.8) and the aliphatic region (δ 0.5-2.1) for the DPL insoluble in the four major fuels examined.

To establish the type of components that are soluble in the fuels, the remaining insoluble fraction was analysed by ^{1}H NMR (fig. 2). Irrespective of the fuel, the ratio of the aromatic region to the other regions in the spectra increases substantially when compared to the samples prior to the blending process. This demonstrates that the majority of fuel soluble components are the aliphatic oxygenates as opposed to the remaining aromatic oligomers in the fuel. Interestingly, the change is more pronounced for the hydrocarbon fuels than for

Fuels used in this study	Maximum blend level of DPL in the fuel (w/w)	Density (15 °C, kg m^{-3})	Energy content (MJ/Kg)	Kinematic viscosity (mm^2 s^{-1})	Cloud point (°C)	Closed cup flash point (°C)
Jet A-1	-	0.796	43.3	4.04 (at -20 °C)	-51	41
ULSP	-	0.724	40.7	0.67 (at 40 °C)	<-60	< 20
Mineral diesel	-	0.844	43.8	2.75 (at 40 °C)	-13	78
RME	-	0.883	40.0	4.89 (at 40 °C)	4.5	> 95
DPL	-	1.232	14.6	28 (at 40 °C)	-21	-
Jet A-1 w/ DPL	17%	0.804	40.2	4.00 (at -20 °C)	-49	33
ULSP w/ DPL	12%	0.750	39.4	0.68 (at 40 °C)	-21	< 20
Mineral diesel w/ DPL	15%	0.840	39.4	2.65 (at 40 °C)	-7	73
RME w/ DPL	16%	0.913	38.7	5.07 (at 40 °C)	-1	> 95

Table 2. Major fuel properties of the depolymerised lignin blends compared to the parent fuels

biodiesel. The insoluble fraction was also analysed by GC-MS (see supporting information). All of the short chain oxygenated species were miscible with the RME and hydrocarbon fuels investigated.

While up to 50% of the esters and aromatic component are potentially soluble in the fuel, the maximum level of DPL that is miscible in the fuels at room temperature varies to between 12 - 17% depending on the type of fuel used (table 2). As this represents the highest proportion that these oxygenated additives would be used in, the properties of these fuel blends were then examined to determine whether the fuels still remained within specification.

Generally short chain esters have densities closer to 1.00 g cm^{-3}, higher than the fuels tested. Accordingly the density of all the novel fuel blends was found to increase slightly on addition of the DPL. The energy density decreases on addition of the oxygenated components for all the fuels tested. The decrease is highest for diesel which is reduced by 10% and lowest for the RME where the energy density is reduced by only 3.2%, though a similar level of DPL is soluble in the fuel. This discrepency in the energy density corresponds with the higher level of aromatic components soluble in the biodiesel and further demonstrates the range of different components from the DPL that are soluble in the different fuels.

Kinematic viscosity is an important metric used to determine fuel quality, especially in the aviation sector. On increasing the biocontent of aviation kerosene to 17% with DPL, the viscosity, measured at -20°C, remains easily within the Jet A-1 limits of 8 mm^2 s^{-1}. Similarly the viscosity of mineral diesel does not change dramatically in increasing the DPL to 16%. While the viscosity of RME increases slightly, presumably due to the different nature of the components soluble in the fuel, the fuel blend is only just out of the limits set out in EN 14 214. This demonstrates that the larger, presumably aromatic, oligomers that increase the viscosity of pure DPL are not present in the final hydrocarbon fuel blends, though are more soluble in the RME which potentially causes the viscosity to increase. While cloud

point is not regulated in the EN 590, 224 or 14 214 for diesel, ULSP or biodiesel respectively, it is an important factor in the Jet A-1 specification. The cloud point of the aviation fuel with DPL does not increase beyond -47 °C, the minimum limit set out in the Jet A-1 standard. Similarly while the cloud point of mineral diesel is increased slightly the cloud point of RME is reduced to below 0 °C.

The flash point of diesel was reduced slightly on addition of DPL, though this was still found to be well above the minimum allowable in EN 590 and ASTM D975. However, the flash point is significantly reduced when the DPL is blended with Jet A-1 aviation fuel and is well below the specified 38 °C. This demonstrates that these oxygenated components would need to be used in far lower concentration than 17%. While the use of oxygenated additives in diesel fuels is well established, the effect of oxygenated additives on the combustion characteristics of aviation fuels is less well understood.

In turbine engines, the combustion characteristics of oxygenated fuels differ appreciably from those of hydrocarbon fuels. It is generally accepted that increased levels of aromatic content within fuels leads to a higher level of particulate matter being present in the exhaust and as such oxygenated fuels typically have lower particulate emissions associated with their combustion, relative to crude oil derived hydrocarbon fuels (Lobo et al., 2011). Fuels with high oxygen contents have been observed to produce lower NO_x emissions, which is of particular importance when considering aviation fuels due to the emissions being produced at an altitude above the tropopause, causing increased damage to the atmosphere relative to NO_x emissions at ground level. It is suggested that the increased oxygen content within the fuel leads to the reduction of the hydrocarbon : oxygen ratio creating a lean combustion mixture. This lean mixture provides an excess of oxygen that is available during combustion thus promoting formation of NO_x. The primary

formation of NO_x is through the thermal (Zeldovich) mechanism and is maximised at stoichiometric combustion mixtures which allow maximum adiabatic flame temperatures (Soares, 2008). The NO_x formation from turbine engines is also increased with increasing time spent by the exhaust gases at high temperature. This thermal formation is combatted in land based technologies by flu/exhaust gas recirculation, however, this is not possible in a jet engine.

Engine exhaust also contains water, formed on combustion which when mixed with the exhaust, cools the gases, reducing the time spent at high temperature, resulting in lower NO_x formation. The water content in the exhaust of oxygenated fuels tends to be higher and therefore has the potential to affect the NO_x emissions, though it should be noted that NO_x formation is primarily dependent on the fuel : air stoichiometry and thus very dependent on the engine control unit. The use of oxygenated fuels also leads to more complete combustion and a reduction of incomplete combustion products such as CO and VOCs (Blakey et al., 2011; Habib et al., 2010). Presumably this would be the major advantage of using oxygenated additives in aviation fuel.

The physical properties of the fuel also have a bearing upon the suitability for use in the aviation sector. The vapour pressure of an aviation fuel is of great importance to its viability. Without sufficient gas phase fuel in the vicinity of the ignition kernel within the combustion section of the engine, ignition becomes difficult. Difficulty in relighting the fuel at altitude after engine flame out is a serious safety consideration (Soares, 2008). Various biofuels have been shown to be more difficult to ignite than conventional jet fuel due to a reduced vapour pressure. However, at high loadings of DPL in fuel the flash point was found to decrease therefore, if an oxygenated component was used in jet fuel then it would need to have a similar volatility to the DPL produced in this study.

While a reduction in NO_x and PM is highly desirable and is potential feasible by the addition of oxygenated additives to aviation fuel, it is only through further engine testing in controlled environments that the minimum blend level and ideal structure of the oxygenates would be fully established. On the other hand, oxygenated compounds including esters, alcohols and ethers, have been investigated as potential additives or blending agents for a wide range of road transport fuels and this is the most likely application for the ozonated lignin. The use of oxygenated species can lead to an increase in the lubricity of a fuel, a change in the ignition delay, a reduction in particulate formation, a reduction in aromatic hydrocarbons and other harmful emissions. The range of components formed over the course of this study did not change the properties of the ULSP, biodiesel or diesel substantially and they seem promising additives for these applications. While this investigation demonstrates the potential of producing additives from DPL, further work is clearly needed into establishing the effect of these additives on the fuel performance. In addition to this testing, further work needs to be invested in tailoring the ozonolysis through further thermal, catalytic or kinetic control to the production of fuel soluble components.

4. Conclusions

Oxygenated phenolics and short chain esters were produced on the ozonolysis of lignin. The ozonolysis of lignin after 24 hours forms a viscous bio-oil with low aromatic content, an energy density of 15 MJ kg^{-1} and a viscosity a magnitude higher than most common fuels. A range of aromatic monomers were also observed at lower reaction times. The oils produced were found to have a partial miscibility with the common fuels tested with up to 50% of the oil being miscible in biodiesel. The main application of the ester-rich fraction was found to be as an additive in road transportation.

Acknowledgements

We acknowledge the EPSRC for funding various aspects of this work, through the Doctoral Training Centre at the Centre for Sustainable Chemical Technologies, Roger Whorrod for his kind endowment to the University resulting in the Whorrod Fellowship in Sustainable Chemical Technologies held by the corresponding author and to Dr. Matthew Jones at the University of Bath for his input into the project

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SUPPORTING INFORMATION

Renewable biofuel additives from the ozonolysis of lignin

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Solvent	Conversion[†] / %	% C	% H	%N	%O
Lignin	-	61	5.5	0.4	29
Ethanol	86	51	5.2	0.4	43
Butanol	38	57	7.3	0.4	34
Hexane	0	-	-		-

Table S1 –Analyses of lignin ozonolysis bio-oils (24 h, 300 mg.h^{-1} ozone); conversions given as % solid reacted; % O calculated from CHN.

Measurement	Units	Result
Net calorific value	Mj/kg	39.99
Density at 15 °C	kg/m^3	883.2
Kinematic Viscosity at 40 °C	mm^2/s	4.89
Flash Point	°C	182.0
Sulphur Content	mg/kg	1.8
Microcarbon Residue 10%	% (m/m)	0.17
Cetane Number		49.5
Water	mg/kg	210
Total contamination	mg/kg	6
Copper corrosion (3 hrs at 50 °C)		1
Oxidation stability (110 °C)	Hours	10.8
Acid number	mg KOH/g	0.18
Iodine number	g/100g FAME	112
Linolenic acid methyl ester	% (m/m)	9.41
Polyunsaturated methyl ester	% (m/m)	<1
Ester content	% (m/m)	97.7
Methanol content	% (m/m)	0.01
Monoglyceride content	% (m/m)	0.57
Diglyceride content	% (m/m)	0.15
Triglyceride content	% (m/m)	0.03
Free glycerol	% (m/m)	<0.01
Total glycerol	% (m/m)	0.17
Sodium	mg/kg	<0.1
Potassium	mg/kg	<0.1
Calcium	mg/kg	<0.1
Magnesium	mg/kg	<0.1
Phosphorus	mg/kg	0.2
Cold Filter Plugging Point	°C	-20

Table S2. EN14 214 test data for the RME used in this study

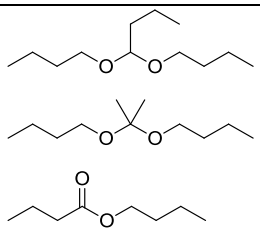
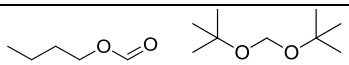
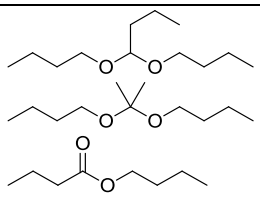
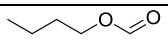
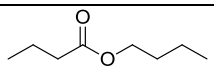
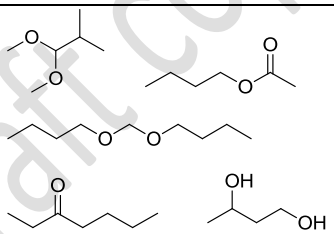
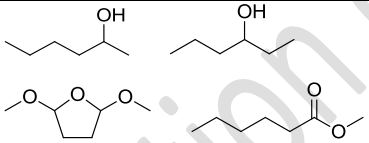
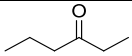
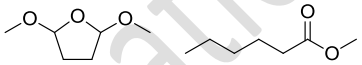
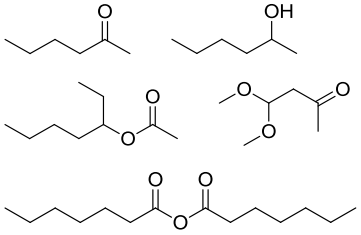
Solvent	Time / h	Products (Major)	Products (Minor)
Butanol	0.5		
Butanol	1	As 0.5 h	As 0.5 h
Butanol	4		
Butanol	24		
Hexane	8		
Hexane	24		
Ethanol	24	-	-
Water	24	-	-

Table S3 The major products produced by the ozonation of the parent solvents without lignin

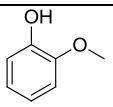
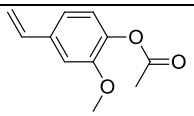
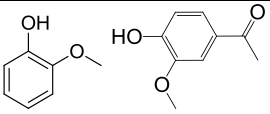
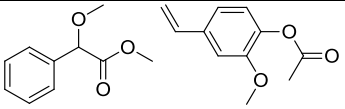
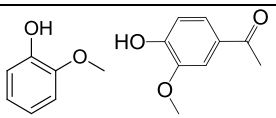
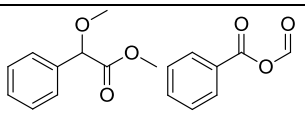
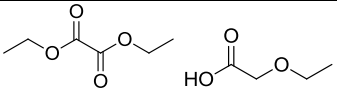
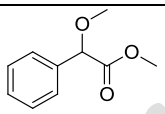
Time / h	Conversion / %	Products (Major)	Products (Minor)
0.5	16		
1	21		
2	27		
8	53		
24	86	See Fig. 3	

Table S4 Products produced by the ozonation of lignin in ethanol

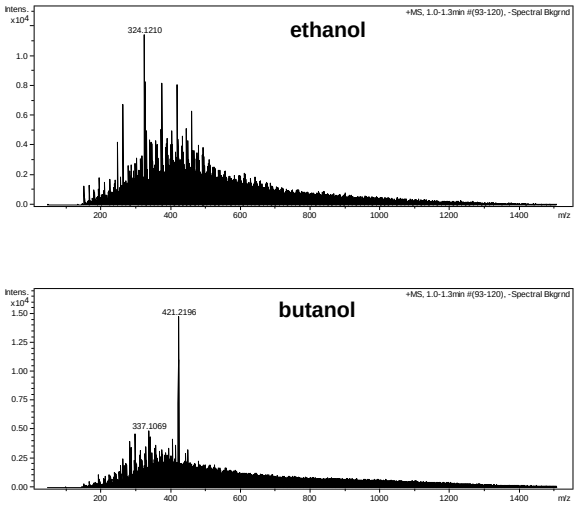


Fig. S1 ESI-MS of the bio-oils formed by the ozonation of lignin over 24 hours with a flow rate of 300 mg.h^{-1} ozone

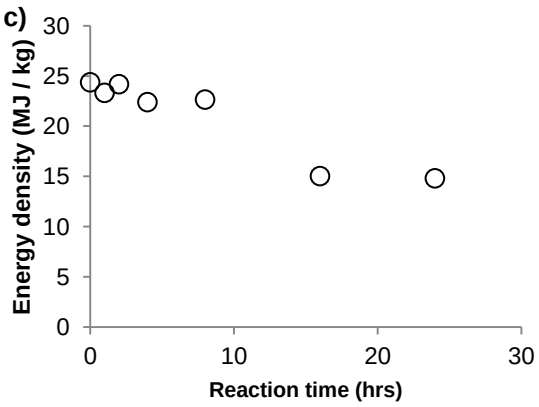


Fig. S2 Energy density of the ozonised lignin in ethanol as a function of reaction time

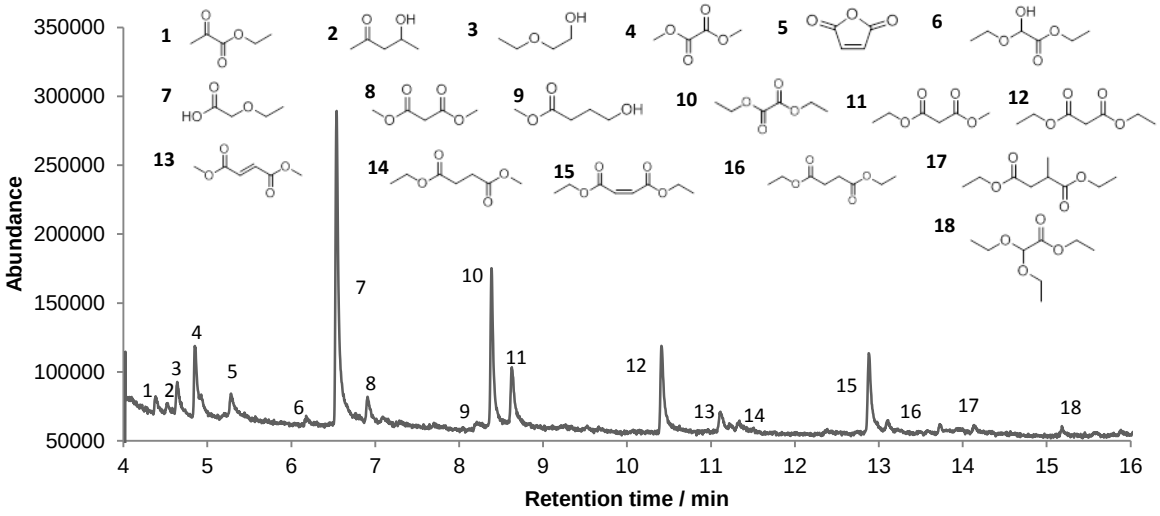


Fig. S3 GC-MS trace of the bio-oil produced from the ozonation of lignin with ethanol over 24 hours, annotated to show the major products.

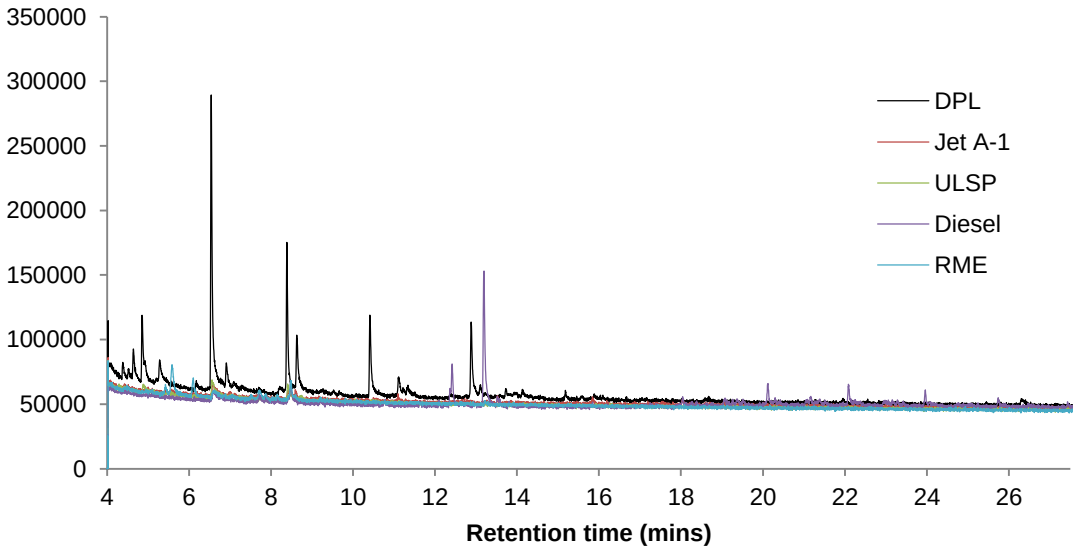


Fig. S4 GC-MS chromatograph showing depolymerised lignin (DPL) and the components insoluble in the DPL. The new compounds observed after the DPL was washed with diesel are hydrocarbons (such as azalene), absorbed from the hydrocarbon fuel into the insoluble component.